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Modification of the Iodimetric Titration Method for the Determination of Bromide and its Application to Mixed Domestic - Industrial Waste Effluents

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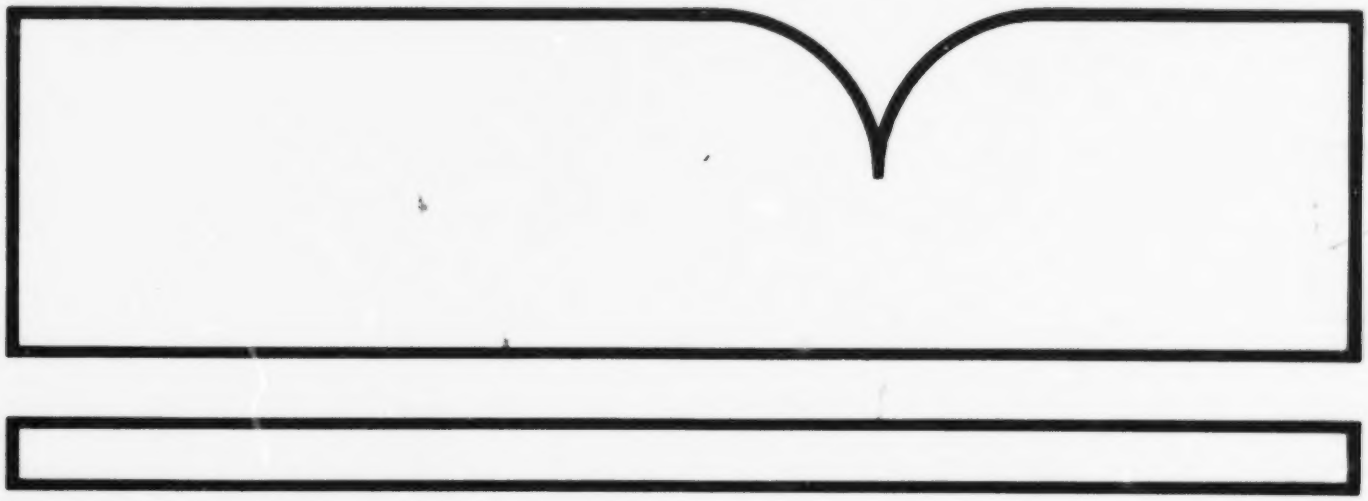

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Modification of the Iodimetric Titration Method for the Determination of Bromide and its Application to Mixed Domestic - Industrial Waste Effluents

Daniel F. Bender

Methods Development and Quality Assurance Research Laboratory, Environmental Protection Agency, National Environmental Research Center, Cincinnati, Ohio 45268, *U.S.A.*

The iodimetric titration method for the determination of bromide involves the observation of various colour changes, making the method unsuitable for use with samples that are highly coloured. A modification is described, which extends the usefulness of the method to highly coloured samples, such as sewage and industrial waste effluents. The obvious substitution of a pH meter for indicators was made and the use of standardised concentrations and amounts of reagents added was incorporated into the method. The procedural steps were studied in order to optimise the sensitivity while minimising interfering side reactions. The modified method was applied to a mixed domestic - industrial waste effluent spiked with bromide and iodide. The experimental details and statistical parameters for samples spiked at different levels are presented.

Ingestion of bromide ion is known to produce physical effects such as bromoderma (skin rashes) and increased spinal fluid pressure and neurological effects ranging from depression and confusion, through hallucination and psychosis, to mental deterioration and coma.[1,2]

The Methods Development and Quality Assurance Research Laboratory of the National Environmental Research Center, Cincinnati, Ohio, is currently developing and evaluating methods of analysis and studying their applicability to the determination of pollutants in industrial waste effluents. The U.S. Environmental Protection Agency guidelines establishing test procedures for the analysis of water pollutants[3] specify ASTM Method D1246-C for bromides.[4] The method involves two titrations. First, the iodide present in the sample is determined by oxidising the iodide to iodate with bromine water and destroying the excess of bromine with sodium formate solution. The amounts of these reagents are not specified in the ASTM procedure,[4] but are determined by visual observation of the subtle yellow bromine colour. The iodate is then made to react with potassium iodide to liberate iodine, which is then titrated with sodium thiosulphate, or an equivalent reductant, using starch as indicator.

Next, the iodide plus bromide is determined by oxidising these ions to iodate plus bromate with hypochlorite, destroying the excess of hypochlorite with sodium formate solution and titrating the iodine released when potassium iodide is added as described above. The bromide concentration is then calculated by difference.

This paper describes the investigation of the ASTM method for bromide when applied to a mixed domestic - industrial waste effluent. Some modifications were necessary in order to compensate for the colour that is often found in such effluents, which masks the indicator changes as well as observation of the subtle yellow bromine colour called for in the original method. The final, iodimetric titration, colour change must be observable, of course. Adjustments in the reagent concentrations were necessary in order to compensate for the loss of reagents, caused by reaction with interferents that consume some reagent without otherwise affecting the final titration.

Experimental

Reagents

Reagents were prepared as directed by ASTM[4] except for the following.

Bromine water. Bromine (0·2 ml) was added to 500 ml of distilled water. The mixture was stirred on a magnetic stirrer with a PTFE-coated follower for several hours, or until the bromine dissolved. The mixture was then stored in a coloured, glass-stoppered bottle.

Methyl red indicator solution. Use of this solution was avoided by using a pH meter.

Potassium hypochlorite solution. This solution was replaced by calcium hypochlorite solution, which is a commercially available material.

Calcium hypochlorite solution. An amount (35 g) of calcium hypochlorite was placed in a 1000-ml calibrated flask. Approximately 800 ml of distilled water were added and the suspension was stirred on a magnetic stirrer for approximately 30 min. The contents of the flask were then diluted to the mark, stirred for a further 5 min, and filtered. The resulting solution was stored in a coloured, glass-stoppered flask.

Sodium thiosulphate solution. Commercially available phenylarsine oxide solution (0·0375 N), standardised with a biiodate primary standard,[5] was used in place of sodium thiosulphate solution; either titrant may be used.

Starch indicator solution. Commercially available amylose indicator (Mallinckrodt) was used.

Procedure

Pre-treatment

A visible excess of calcium oxide was added to a 400-ml sample in order to eliminate the effects of iron, manganese and organic matter, as has been described.[4] The solution was vigorously stirred for approximately 15 min and filtered, the first 75-ml portion of filtrate being discarded. In practice, samples up to 3 l were pre-treated in this manner.

Iodide determination

A 100-ml volume of pre-treated sample containing not more than 20 mg l^{-1} of iodide, or a fraction thereof diluted to 100 ml, was placed in a 150-ml beaker. By use of a magnetic stirrer and a pH electrode, sulphuric acid (1 + 4) was added dropwise until a pH of approximately 7 (or slightly less) was obtained. The solution was then transferred to a 250-ml, wide-mouthed conical flask and the beaker washed with distilled water; the washings were added to the conical flask. Sodium acetate solution (15 ml) and 5 ml of acetic acid (1 + 8) were added and the flask was swirled to mix the solutions. Forty millilitres of bromine water were added and the solutions mixed and allowed to stand for 5 min. Sodium formate solution (2 ml) was added and again the flask was swirled to mix the solutions. The sides were washed down and the flask was allowed to stand for an additional 5 min, a gentle stream of nitrogen being blown in to displace any bromine fumes. Because there was no indication of the presence of iron upon cooling (formation of a precipitate),[4] the addition of potassium fluoride was not necessary. The solution was then titrated as described below under *Titration.*

Bromide plus iodide determination

A 100-ml volume of pre-treated sample containing not more than 20 mg l^{-1} of bromide plus iodide, or a fraction thereof diluted to 100 ml, was placed in a 150-ml beaker and 5 g of sodium chloride were added. Dissolution of the sodium chloride was effected by using a magnetic stirrer. When the sodium chloride had dissolved, the pH was adjusted to approximately 7 by adding hydrochloric acid (1 + 4) dropwise; the solution was then transferred, with washing, into a wide-mouthed conical flask. Calcium hypochlorite solution (20 ml), a further 1 ml of hydrochloric acid (1 + 4) and approximately 0·2 g of calcium carbonate were added. The solution was heated to boiling on a hot-plate and boiling maintained for an additional 8 min. The flask was removed from the hot-plate, 4 ml of sodium formate solution were added, then the sides of the flask were washed down with distilled water; it was returned to the hot-plate and the solution was allowed to boil for an additional 8 min. The sides of the flask were occasionally washed down when evaporation produced a residue on the sides. The flask was then allowed to cool. As, upon cooling the solution, there was no indication of the presence of iron (formation of a precipitate),[4] the addition of potassium fluoride was not necessary. Several drops of sodium molybdate solution were added and the sample was titrated as described below under *Titration.*

Titration

Approximately 1 g of potassium iodide was added to the flask and dissolved by gently swirling the flask. Ten millilitres of sulphuric acid (1 + 4) were added and the flask was set aside in the dark for 5 min. The solution was then titrated with the 0·0375 N phenylarsine oxide solution, the amylose indicator being added as the end-point was approached. The blue colour usually reappeared on standing, but this was disregarded.

Calculations

The calculations were performed as described in the ASTM standard method[4] with the exception that the volume of titrant used by a distilled water blank must be subtracted from the volume of titrant used in the bromide plus iodide determination.

The equation thus becomes:

$$Br^- \text{ (mg l}^{-1}) = 13\,320 \left[\frac{(A - B)C}{D} - \frac{(E - F)G}{H} \right]$$

where A is the volume (ml) of phenylarsine oxide needed to titrate the sample for bromide plus iodide; B, the volume (ml) of phenylarsine oxide needed to titrate a distilled water blank that has been treated with the same reagents as the sample for bromide plus iodide; C, the normality of the phenylarsine oxide solution used to titrate the sample and blank for bromide plus iodide; D, the volume of samples taken (100 ml or a fraction thereof) to titrate the bromide plus iodide; E, the volume (ml) of phenylarsine oxide needed to titrate the iodide in the sample; F, the volume (ml) of phenylarsine oxide needed to titrate a distilled water blank that has been treated with the same reagents as the samples in which the iodide was titrated; G, the normality of the phenylarsine oxide used to titrate the iodide in the sample and blank; and H, the volume of samples taken (100 ml or a fraction thereof) for the iodide titration.

Results and Discussion

Pre-treatment

A synthetic sample containing approximately 10 mg l^{-1} of iron(III), 10 mg l^{-1} of manganese(II), 25 mg l^{-1} of bromide and 25 mg l^{-1} of iodide ions was pre-treated and then analysed to determine bromide and iodide. The formation of a precipitate upon cooling, which would have indicated the continued presence of iron, was not observed. The pre-treatment was therefore shown to be effective, as stated by ASTM,[4] and was not studied further.

Iodide determination

The use of a pH meter was substituted for the acid - base indicator because industrial waste effluents are often highly coloured. In addition, the presence of colour in the sample can make the various yellow bromine colours (which serve as an indication of how much bromine to add and how much sodium formate is required to quench the bromine) impossible to observe. Therefore, specified volumes of bromine water and sodium formate solution were substituted. The amounts of these reagents required for a stoicheiometric reaction with 25 mg l^{-1} of bromide or iodide were calculated and an excess of bromine was added. It was found that if the bromine water was too concentrated, an unreproducible blank resulted. It was also found that when a sewage sample was used, an interference consumed some of the bromine so that a further slight excess had to be added; the amount of bromine water chosen for the method was ascertained by trial and error.

Bromide plus iodide determination

The required amounts of calcium hypochlorite and sodium formate solutions were determined by using considerations similar to those for the iodide determination. There is a definite titratable blank, therefore a distilled water blank determination must be carried out with each set of samples.

Titration

The starch - iodine titration is commonly used for dissolved oxygen determinations.[5] Whichever titrant or indicator is most convenient can be substituted in the method; phenylarsine oxide and amylose indicator were used in this study because they were readily available. The procedure for preparing sodium thiosulphate and starch indicator is described by ASTM.[4] For a routine analytical application, it is suggested that 0·0075 N phenylarsine oxide should be used. This concentration would provide a larger volume of titrant in the concentration range of bromide and iodide ions suggested.

Analytical parameters

Tables I and II show the standard deviation and accuracy (percentage recovery) for mixed domestic - industrial waste samples from the Cincinnati, Ohio, Sewage Treatment Plant with a wide range of iodide and bromide concentrations. In each instance seven replicates were run. The results for the iodide determination are included because the results had to be obtained in order to complete the bromide calculation.

TABLE I

STATISTICAL DATA ON BROMIDE DETERMINATION USING SPIKED AND UNSPIKED SAMPLES OF MIXED DOMESTIC AND INDUSTRIAL WASTE EFFLUENTS

Spike*/mg l^{-1}	Theoretical total concentration/ mg l^{-1}	Found total concentration/ mg l^{-1}	Standard deviation (s)	Coefficient of variation,† per cent.	Recovery,‡ per cent.
0	—	0·3	0·13	43	—
2·5	2·8	2·7	0·37	14	96
5·0	5·3	4·4	0·38	9	83
10·0	10·3	10·0	0·44	4	97
20·0	20·3	20·1	0·42	2	99

* The amount of spike that is listed was added to the sample, which already contained some halides.

† Coefficient of variation $= \frac{s}{\text{found}} \times 100$.

‡ Recovery, per cent, $= \frac{\text{found}}{\text{theoretical}} \times 100$.

The sample used for determining the statistical parameters had a natural concentration of 0·3 $\pm$ 0·13 mg l^{-1} of bromide and 1·6 $\pm$ 0·23 mg l^{-1} of iodide, as is shown in Tables I and II. The standard deviations and coefficients of variation for the various levels of spiked sample are shown. As expected, the method becomes more precise as the concentration of the spike increases. The percentage recovery, which is an indication of the accuracy, was generally between 92 and 99 per cent.; however, occasionally levels as low as 80 per cent. were obtained. Although running samples spiked at these levels again produced results at a level above 90 per cent., the values shown in the tables were recorded in order to illustrate that lower yields are occasionally obtained, that spiking is necessary to judge the nature of the sample and also because particular results for yield were obtained from the same spiked sample as those for standard deviation and coefficient of variation.

TABLE II

STATISTICAL DATA ON IODIDE DETERMINATION USING SPIKED AND UNSPIKED SAMPLES OF MIXED DOMESTIC AND INDUSTRIAL WASTE EFFLUENTS

Spike*/mg l^{-1}	Theoretical total concentration/ mg l^{-1}	Found total concentration/ mg l^{-1}	Standard deviation (s)	Coefficient of variation,† per cent.	Recovery,‡ per cent.
0	—	1·6	0·23	14	—
2·5	4·1	3·3	0·17	5	80
5·0	6·6	6·4	0·10	2	97
10·0	11·6	11·2	0·06	0·5	97
20·0	21·6	19·8	0·50	3	92

* The amount of spike that is listed was added to the sample, which already contained some halides.

† Coefficient of variation $= \frac{s}{\text{found}} \times 100$.

‡ Recovery, per cent. $= \frac{\text{found}}{\text{theoretical}} \times 100$.

The method described by ASTM[4] is capable only of determining levels of bromide above 50 mg l^{-1} because it involves observing subtle changes in the yellow colour of bromine. It permits the use of highly variable amounts of bromine and sodium formate, the bromine quencher, thereby ensuring sufficient reagent concentration without excess. Excess reagent

concentration produces a high blank. As these colour changes are not observable in a coloured sample, the modification described in this paper involves the use of standard concentrations of the reagents in order to ensure that there is a sufficient amount of reagent, yet not so great an excess as to produce a high blank. This modification produces a limitation on the upper limit of the range.

The range 2–20 mg l^{-1} was determined by calculating the amounts of the reagents (bromine water and calcium hypochlorite solution) that were necessary to determine a maximum of 25 mg l^{-1}, then an excess was added to compensate for reagent consumed by interferents. If a value greater than 20 mg l^{-1} was observed the sample was diluted and run again to make sure that the value was not actually above the upper limit. Distilled water was deliberately spiked at the 50 mg l^{-1} level and analysed using reagent concentrations calculated for a 25 mg l^{-1} maximum. A result of 25 mg l^{-1} was obtained, as anticipated. The lower range limit was chosen because of the observation that the bromide - iodide determination gave a blank of approximately 0·5 ml of titrant and the conviction that approximately 1·0 ml of titrant is necessary for the result to be significantly different from that of the blank.

Conclusion

The bromide method as presented is applicable to highly coloured samples in the range 2–20 mg l^{-1} of bromide when the iodide concentration is also in that range or lower. Samples that are more concentrated in either component must be diluted. Spiked samples should be run with each sample type because of the possibility of interferences that could consume the reagent and therefore affect the results.

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